CARBON NANOTUBE FIELD EMITTERS FOR MINIATURE MASS SPECTROMETERS AND NANOKLYSTRONS

Final Report

JPL Task 1018

Harish M. Manohara, Microwave Experiment Systems and Technology Section (386)
Peter H. Siegel, Microwave Experiment Systems and Technology Section (386)
Michael Hoenk, Section 384
Murray Darrach, Section 323
Ali Husain, California Institute of Technology
James Hone, California Institute of Technology
Michael Roukes, California Institute of Technology
Axel Scherer, California Institute of Technology

A. OBJECTIVES

The development of a low-operating-voltage, high-current-density electron source is essential for the miniaturization of mass spectrometers and vacuum-tube sources of terahertz radiation for future lightweight, low-cost, robotic space missions. Carbon nanotubes have shown great promise in fulfilling such an electron source requirement [1]. The goal of this research effort is to conduct a systematic study of field-emission properties of different types of carbon nanotubes, and then develop grid-integrated carbon-nanotube (CNT) field-emission arrays for use as ionizers in miniature mass spectrometers [2] and as high-current-density electron sources in the *nanoklystron*-- a micro-tube source of THz radiation [3]

Objectives of this proposal were to 1) fabricate dense, unidirectional carbon nanotubes with monolithic integrated grids, 2) test the field-emission characteristics of these nanotubes in a generic emission-test system, built using this grant, which can also be used for assembling and packaging nanotubes with micro devices, and 3) demonstrate the use of these new emitters in prototype compact gas ionizers and nanoklystrons. The proposal represents a multidisciplinary effort spanning four different research groups at JPL and Caltech, drawing from and merging their combined strengths and device needs.

B. PROGRESS AND RESULTS

By the end of the project period, almost all of the setout milestones had been accomplished except one of them, which is to test the CNT source in a nanoklystron. This was not possible owing to fabrication and integration complexities that had to be sorted out and that needed more time. Table 1 below compares the original task-implementation plan with the tasks accomplished at the end of the project period (black bars indicate originally planned milestone periods, and gray bars indicate the accomplished milestones).

***Table 1**. Final status of the project with respect to the original task implementation plan*

Tasks	First 6 Months	Second 6 Months	Third 6 Months
SWNT and MWNT growth on plain and patterned substrates			
Field emission test system construction			
Fabrication of stand-alone grids for initial testing			
First field emission tests			
Integration of grid on SWNTs and MWNTs			
Second field emission tests			
Possible assembly of nanotubes into a Nanoklystron prototype			
Designing of field emission source for miniature gas ionizers			

1. Science Data

Systematic study of field emission was conducted on single-walled nanotubes (SWNTs) and random multi-walled nanotubes (MWNTs). SWNTs were fabricated at 900°C and MWNTs were fabricated at 600°C in tube furnaces using standard CVD techniques. The tube density was higher in the case of MWNT samples. Low-density, disordered, as well as highly dense, vertically aligned varieties of MWNTs (Figure 1) were tested. As previously reported [4], high-density samples suffered from enhanced screening effect, thus decreasing their total electron emission. The tests were conducted in a diode mode with an Indium Tin Oxide (ITO)-coated glass slide as the anode (Figure 2). The anode was also coated with a fluorescent phosphor layer to visually identify the emission sites and their distribution on each sample. ITO-coated anode also acts as a global anode, highlighting the hotspots on a sample, which are invariably present due to non-uniform lengths of CNTs. This is explained in detail further down.

Figure 3 shows field-emission curves for all the samples tested. The curves follow the Fowler-Nordheim formula {$ln\ (I / V^2) = ln\ (a) – b / V$, where, I: emission current, V: biasing voltage, and a, b are constants}, as can be seen in the curves shown in the inset of Figure 3. SWNTs showed a maximum current of ~1.18 mA at 30.7 V/µm. The highest-emission currents were measured from disordered, less-dense MWNTs and were found to be ~0.63 mA @ 3.6 V/µm (sample 1) and ~3.55 mA @ 6.25 V/µm (sample 2). The high-density vertically aligned MWNTs (vertically aligned because of the high packing density), showed low field emission as predicted: 0.31 mA @ 4.7 V/µm. This low-emission current from the SWNTs can be attributed to very low nanotube density in the sample area. All samples were grown on a template of ~7 mm^2 (Figure 1 (a)), and although the entire area was under the applied field, Figure 4 shows that the actual emission was occurring from only a few sites with a much smaller effective area. These are the hotspots mentioned above. They result from the electrostatic screening effect that occurs due to non-uniform lengths of CNTs. The taller nanotubes concentrate the field and screen the shorter ones from participating in emission. This problem can be corrected by using an integrated grid that localizes the electric field to a smaller area, thus allowing locally taller tubes to emit electrons.

It was observed that, over time, all samples exhibited large variations in emission current at fixed voltage. For the MWNT samples at certain higher fields, the range of current variation was as high as 60%. Also, high fields caused explosive erosion of the sample surface where the nanotubes were actually thrown off (Figure 5). These early field-emission results steered the project to focus on the development of MWNTs as the most suitable candidates for high-density electron emission.

A novel process was developed to integrate grids with nanotubes. The uniqueness of the process is that the integration takes place post-nanotube fabrication, which is not reported anywhere in literature. Figure 6 shows a process flowchart for post-nanotube growth integration of grids as well as SEM micrographs of integrated gold grids. At the time of project completion, few problems with the grid strength and integrity during field-emission tests were being corrected. We could not complete a field-emission test with integrated grids in time for this report, but the process is well developed and will be supported for continued development under a different NASA Code-R program.

A nanotube-emitter template was fabricated with MWNTs as shown in Figure 7 (a) for use with a miniature mass spectrometer. First tests of introducing CNT-based cold-cathode electron sources into the Atomic and Molecular Collisions (A&MC) team's engineering model of the flight QMSA (quadrupole mass spectrum analyzer) mass spectrometer were conducted. The QMSA is comprised of two sections: the ionizer and the mass analyzer. Gases are admitted into the QMSA and ionized by electron impact, with the resultant ions focused into the input apertures of the mass analyzer. The mass analyzer is 5 cm (long) x 3 cm (diameter) and consumes 12 W of power. There are considerable merits in pursuing an ionizer based upon a patterned array of carbon nanotubes to replace heated filament. The foremost reason is a reduction in power by at least a factor of 100. Also, in the case of the QMSA, a nanotube ionizer would result in mass and size reduction of at least a factor of two. Figure 7 (b) shows the miniature mass spectrometer with CNT-emitter template assembled instead of the thermionic filament. This assembly was put inside a UHV (ultra-high vacuum) chamber and tested. At present, a hot cathode is used to generate ~ 10 mA of current and then couple ~1% of it through quadrupoles for mass spectral analysis. In our first test, we were able to produce a current of ~ 0.5 μA at the emitter region and couple ~ 2 nA of that to the quadrupole. At this point, the circuit shorted due to wearing out of the insulator layer. The setup has since been modified to include an additional insulating film of 5 μm-thick Teflon. At the time of this report, the setup was still waiting to be tested.

2. Other Results

As planned in the original proposal, a multipurpose ultra-high-vacuum (UHV) chamber was constructed with funds from this and one other proposal (code R- Nanoklystron) for field-emission testing as well as for the nanoklystron-device assembly and testing. Figure 8 shows a photograph of the test chamber, which is currently being used for field-emission testing.

C. SIGNIFICANCE OF RESULTS

This task has initiated an important developmental effort of realizing a high-current-density electron source based on field-emission phenomena. This development will have significant impact on high-resolution heterodyne spectroscopy using THz radiation (nanoklystron), on the chemical analysis of complex environments, and on the effort to safeguard astronaut health through environmental monitoring (miniature mass spectrometer). Both of these instruments are of great significance for future NASA missions.

The results indicate that low-emission-threshold voltage is already possible, and can be further improved by adding extraction grids. Also, the measured current density is already suitable for preliminary tests with the miniature mass spectrometer. Results from this developmental work have pointed the way towards understanding the nanotube density effect on emission efficiency, and have led to work to realize density-modulated nanotube samples that can generate very high current densities (of the order of several hundreds to a kiloampere per sq. cm). A new process to integrate extraction and focusing grids post-nanotube-fabrication offers the unique advantage of being insensitive to different nanotube-synthesis procedures.

D. FINANCIAL STATUS

The total funding for this task was $156,500, all of which has been expended.

E. PERSONNEL

Wei Lien Dang (SURF student from Caltech)

F. PUBLICATIONS

[1] *(Invited)* H.M. Manohara, Wei Lien Dang, Michael Hoenk, Ali Husain, Peter H. Siegel, Axel Scherer, "Field Emission Testing of Carbon Nanotubes for THz Frequency Vacuum Micro-Tube Sources ," *SPIE Micromachining and Microfabrication: MF02 Reliability, Testing, and Characterization of MEMS/MOEMS III*, San Jose, CA, January 23-25, 2003.

[2] H. Manohara, P.H. Siegel, C. Marrese, B. Chang, J. Xu, "Fabrication and Emitter Measurements for Nanoklystron: A Novel THz Micro-Tube Source," *Third IEEE International Vacuum Electronics Conference- IVEC 2002*, Monterey, CA, April 23-25 (2002)

G. REFERENCES

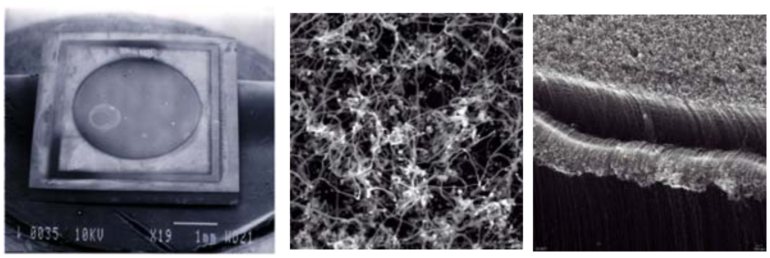
[1] Jean-Marc Bonard *et* al, “ Field emission from carbon nanotubes: first five years,” *Solid-State Electronics*, Vol. 45, pp. 893-914 (2001)

[2} *Private communication with* Murray Darrach, Section 323, JPL.

[3] P. H. Siegel, T.H. Lee, J. Xu, “The Nanoklystron: A New Concept for THz Power Generation,” *JPL New Technology Report*, NPO 21014, Mar. 21 (2000)

[4] L. Nisson *et al*, “Scanning field emission from patterned carbon nanotube films,” *Applied Physics Letters*, Vol. 76, No. 15, pp. 2071-2073 (2000).

H. APPENDIX: *FIGURES*



(a) b) (c)

Figure 1. (a) Carbon-nanotube template for field-emission testing, (b) disordered, less-densely-distributed MWNTs, (c) vertically aligned, highly dense MWNTs.

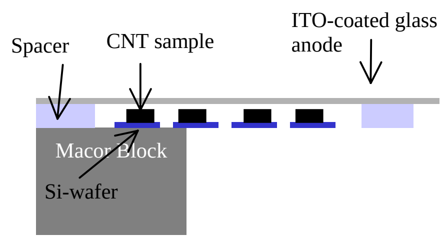


Figure 2. Measurement set-up inside a high vacuum chamber

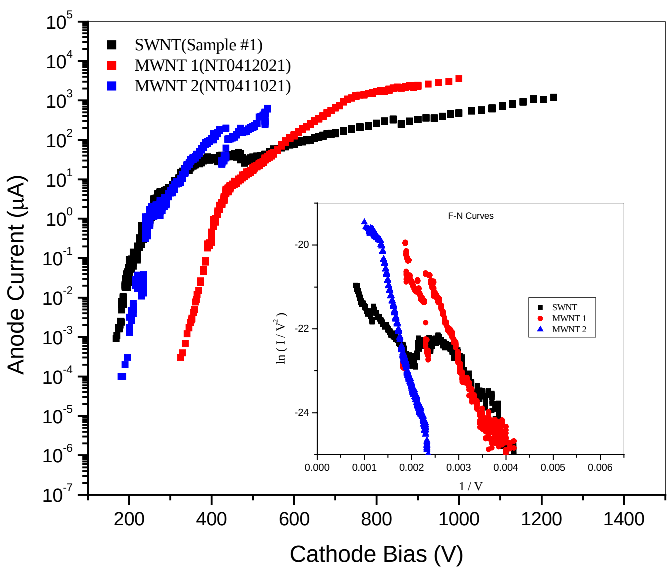


Figure 3. Field-emission curves for SWNTs and MWNTs (two samples) shown at the actual tested voltage biases. The anode-cathode gaps were ~ 40 μm, 150 μm and 160 μm respectively. The inset shows the Fowler-Nordheim curves.

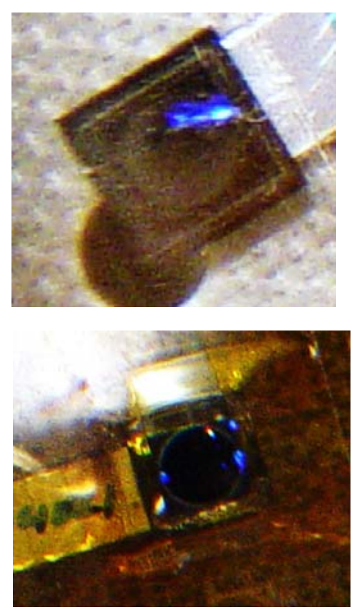


Figure 4. Fluorescence on the anode, corresponding to emission sites on CNT samples, shows spotty and scattered field emission.

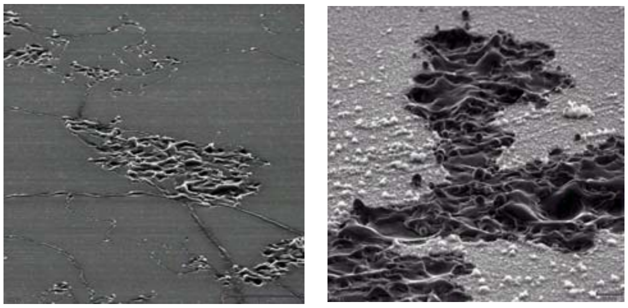
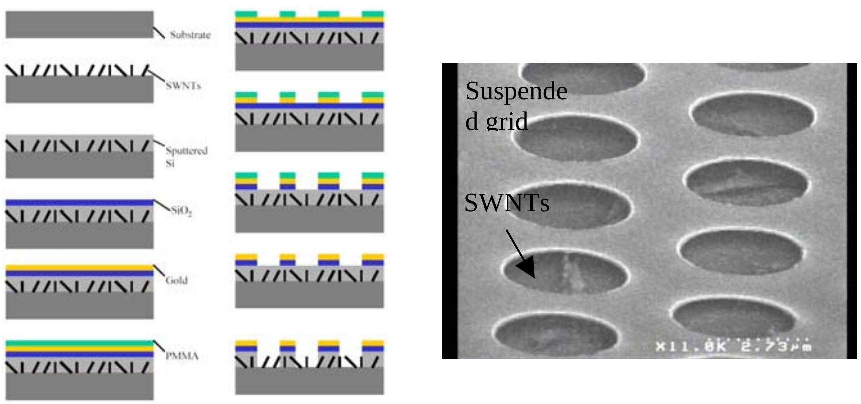


Figure 5. Damaged CNT sample surface due to high field effects. The nanotubes have been thrown off due to surface erosion.



(a) **(b)**

Figure 6. *(a) Process flow chart of grid integration post nanotube fabrication, (b) SEM micrograph of suspended grid structure with SWNTs grown in the center (Wei Dang and Ali Husain of Caltech)*

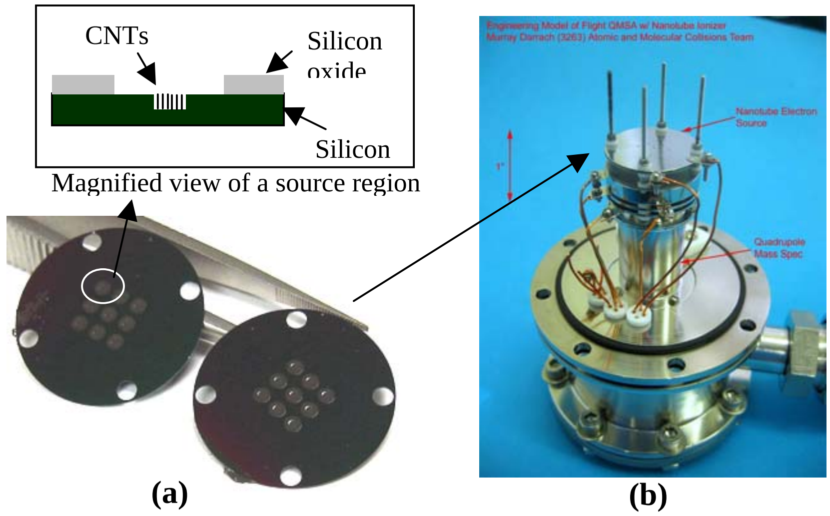


Figure 7. *(a) Carbon-nanotube-based field-emission electron source templates for miniature quadrupole mass spectrometer, (b) Engineering model of the flight QMSA assembly with CNT-emitter template integrated into it in place of hot-filament electron source.*

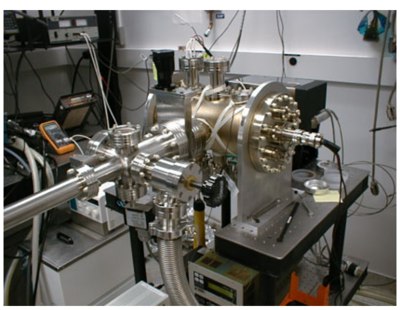


***Figure 8**. UHV chamber for field-emission testing and for nanoklystron assembly and testing*